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(58) Field of Search

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(54) Abstract Title

Diamond containing cermet

(57) A cemented carbide composite article formed from particles of tungsten carbide and particles of diamond dispersed in a cobalt matrix, wherein the diamond content does not exceed 2 % by weight. Preferably the diamond particles are synthetic industrial diamonds, each having a diameter less than 15 microns and each being substantially spherical. The article preferably has a hardness between 1600-1800 HV and forms part of a cutting insert. The article is made by adding diamond particles to a blend of tungsten carbide and cobalt grains, pressing and then sintering. Sintering may be performed by heating in a reducing atmosphere (e.g. for up to 12 hours at 750°C in a hydrogen atmosphere), cooling and subsequently heating in a vacuum furnace (e.g. for up to 16 hours at 1375°C). The blend of WC and Co may be ball milled with the diamonds prior to sintering.

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Metal Carbide Composite

Description

The present invention relates to metal carbide composite materials and, in particular, to cemented tungsten carbide cutting elements that are brazed or welded onto the tips of fluted drills or around the circumference of saws. These types of tools are used in processing of natural stone and concrete as well as in general engineering materials.

Cutting inserts and segments made from cemented carbides are well known. Cemented tungsten carbide is produced by blending micron or sub-micron sized tungsten carbide (WC) powders with, in the majority of cases, ultra-fine cobalt (Co) powders. Cemented carbide is normally produced in weight ratios of 85%-99% WC to 1%-15% Co, depending on the intended application.

The constituent WC and Co powders are often blended with other elemental or carbide additions such as titanium carbide or tantalum carbide to enhance the performance of the material. The mixture is then ball milled for a period of 24 to 96 hours in the presence of a solvent/lubricant such as acetone. This is usually carried out in a tungsten carbide container using tungsten carbide balls. The ball milling time and other operating parameters are dependent on the final product requirements and its intended application.

After the ball milling operation, the product is dried in a vacuum and the solvent condensed and re-circulated. The resulting blend is then referred to as "grade powder".

The grade powder is subsequently formed into the desired shape. Typically this is done by a cold press compaction of the powder. However, it may also be formed by compacting the powder in an isostatic press or by extrusion. The resulting article is commonly referred to as a "green compact".

Next, the compact undergoes a sintering cycle. In a widely used traditional sintering cycle, the compact is placed in a furnace under a reducing atmosphere and heated to a temperature of up to 750 degrees centigrade for a period of between 4 to 24 hours, largely depending on the size and shape of the compact. During this process, the solvent/lubricant, other organic compounds and trapped oxygen are removed from the compact. It is then cooled before being transferred to another furnace where it is heated under vacuum to a temperature of up to 1600 degrees centigrade over a period of 12 hours, the exact temperature and time being dependent on the size, shape and composition of the component.

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In an alternative sintering cycle known as a Combined Cycle Operation, a specially designed furnace is used as both a reducing furnace and a vacuum furnace at temperatures over 750 degrees centigrade. Although the cycle time in the Combined Cycle is longer and the capital cost of the furnace is higher, this cycle is more cost effective in the long term as the components do not need to be heated twice. However, some doubt persists about the quality obtained using a combined cycle process as opposed to the more traditional sintering technique.

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The temperatures employed in the sintering process are high enough to cause the cobalt to flow so that it fills the voids between the tungsten carbide grains and coats them. When the cobalt solidifies, it cements the grains together to form a dense composite that has excellent mechanical and physical properties such as high abrasion resistance, wear resistance and toughness. It therefore makes an ideal insert for cutting tools.

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Another type of conventional cutting insert is made from polycrystalline diamond (PCD). A PCD layer is produced by the sintering or "intergrowth" of diamond particles, in a binder phase, often cobalt. The sintering process is carried out in specially designed presses that are capable of exerting very high pressures in the region of approximately 6Gpa at temperatures of the order of 1500 degrees centigrade. Under these conditions the diamond is dissolved into the binder phase as carbon and then precipitated as diamond at the areas where the diamond particles touch. The result is a mass of diamond in the form of a layer that can be

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subsequently processed into cutting inserts. PCD can be produced in a freestanding form but is more frequently produced with an integral cemented carbide substrate, to facilitate brazing the PCD layer onto tool assemblies.

5 It is important to note that the main constituent of the PCD layer is the diamond particles and that substantially all the diamond particles are bonded to adjacent diamond particles. The metal is present in only small quantities, merely to facilitate the sintering process and act as a binder so that the diamond layer bonds to the cemented carbide substrate.

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PCD cutting inserts offer many advantages over standard cemented carbide inserts and can be used for machining very abrasive non-ferrous and non-metallic materials. PCD has a very high abrasion resistance and is very hard compared with cemented carbide or ceramic materials. In many applications PCD tool life can exceed
15 cemented carbide or ceramic tools by well over 100 times.

Despite the wear resistance and enhanced cutting performance of PCD inserts, they suffer from a number of drawbacks. In particular, PCD has a relatively low impact strength as a result of its high elastic modulus and brittleness. For this reason, PCD
20 cutting tips are rarely used in fluted drill configurations, particularly if the work piece material itself has a high hardness. Furthermore, PCD manufacture and processing is relatively sophisticated and so resulting tools are significantly more expensive than tools made from conventional cemented carbide.

25 Another problem surrounds the interface between the PCD layer and the integral cemented tungsten carbide substrate that supports it. Due to the difference in the co-efficient of thermal expansion between the diamond layer and the cemented carbide layer, care must be taken during the brazing of the insert to the tool assembly otherwise different material contraction or expansion rates can cause the
30 PCD layer to crack.

It is an object of the present invention to overcome or substantially alleviate the problems associated with conventional PCD composites such as those described

above. The invention also seeks to provide a diamond/cemented carbide composite that exhibits properties, and has a life span, that is intermediate to that of currently available cemented carbide compacts and PCD, whilst maintaining the relative ease by which cemented carbide compacts are manufactured.

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According to the present invention, there is provided a cemented carbide composite article formed from particles of tungsten carbide and particles of diamond dispersed in a matrix of cobalt, wherein the percentage weight of diamond particles in the article does not exceed 2%.

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Preferably, the particles of diamond each have a diameter less than 15 microns. Although in an even more preferable embodiment, the particles of diamond each have a diameter between 2 and 10 microns.

15 Advantageously, the particles are substantially spherical.

In a preferred embodiment, the composite article has a hardness of between 1600 and 1800HV.

20 Conveniently, the proportion of tungsten carbide (WC) to Cobalt (Co) is 9:1 and the compact has a hardness of approximately 1770HV.

In a preferred embodiment, the diamond particles are synthetic industrial diamond powder.

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Advantageously, the diamond particles are uniformly dispersed throughout the article.

The present invention also relates to a cutting insert formed from the composite article according to the invention.

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The present invention also provides a method of manufacturing a composite article according to the invention comprising the steps of adding diamond particles to a

blend of tungsten carbide and cobalt grains at a percentage weight not exceeding 2% of diamond and pressing and sintering the resulting powder to form the compact.

5 In a preferred embodiment, the sintering step comprises the steps of:

- a) heating the resulting compact in a reducing atmosphere;
- b) cooling the compact and,
- c) subsequently heating the compact in a vacuum furnace.

10 Preferably, the method includes the step of simultaneously precipitating cobalt and tungsten carbide alloyed together to form a pre-mixed and pre-alloyed blend of tungsten carbide and cobalt grains prior to mixing the blend with diamond particles.

The blend of WC and Co is preferably ball milled with the diamond particles prior
15 to sintering.

The ball milling step is conveniently carried out for 72 hours.

In a preferred embodiment, step (a) includes the step of heating the article to 750°
20 C in a reducing Hydrogen (H₂) atmosphere.

Preferably, the composite article is heated for 12 hours depending upon the shape, dimensions and the weight of the component.

25 In a preferred embodiment, step (c) involves heating the article in a vacuum furnace up to 1375 degrees centigrade using a pre-assigned heating cycle.

Preferably, the article is heated up to 16 hours depending upon the shape, dimensions and the weight of the component.

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The method steps of the present invention are advantageously carried out at atmospheric pressure.

The Applicants have realised that by doping the cemented metal carbide with only a very small percentage by weight of diamond particles, the temperature at which the composite is sintered can be reduced with no loss of integrity of the material as a result, i.e. there is no apparent reduction in material hardness or relative density
5 obtained. Furthermore, the reaction between the diamond particles and the cobalt/tungsten carbide matrix increases the hardness and the wear resistance of the resulting inserts.

To date, the addition of small quantities of diamond has not been considered viable
10 as it is universally expected in the industry that two reactions would take place. Firstly, the surface of the diamond would oxidise to form carbon dioxide. Secondly, the remaining diamond, in such a small concentration, would revert to graphite under the influence of the temperature/time cycle and in the presence of cobalt or any other catalytic metal.

15 More specifically, diamond is a met-stable allotrope of carbon that can be synthesised using high temperature (approximately 1500 degrees centigrade) and high pressure (approximately 6Gpa), in the presence of a metallic catalyst such as cobalt. However, a skilled person in the field of technology concerned would
20 expect, as a the result of heating diamond particles in the presence of catalyst and without the application of pressure, the back reaction to occur so the diamond would be converted to graphite which presents itself in the form of graphite pools. Therefore, a skilled person appreciates that the addition of small amounts of diamond in the concentrations proposed would be a complete waste of time.
25 However, the Applicants have determined that the expected result is incorrect and that a composite compacted powder of tungsten carbide and cobalt with diamond particles in a weight concentration of 2% or less can be sintered without any apparent signs of the carbon reverting from diamond back to graphite.

30 In addition to increasing the wear resistance and hardness of the resulting inserts, the sintering temperature required to manufacture them can be reduced by approximately 100 degrees centigrade. This is a significant advantage as it reduces

energy costs as well as simplifying the requirements of the furnace used to produce the insert.

5 Embodiments of the present invention will now be described, by way of example only.

A pre-mixed/pre-alloyed tungsten carbide and cobalt blend was taken as a base material. This material differs from a standard tungsten carbide and a cobalt powder mix in so much as it is simultaneously precipitated cobalt and tungsten carbide
10 alloyed together. This powder has a grain size very much smaller than that of conventional tungsten carbide and cobalt powder and is on the nanometre scale. A pre-mixed/pre-alloyed blend is not commonly used in the manufacture of cemented carbide as it is more expensive than the standard tungsten carbide and cobalt mix and the additional costs are not justified when compared with only the small
15 improvements seen in the properties of the compacts produced.

Ball milling of this premixed/pre-alloyed WC and Co and diamond powder was then undertaken for 72 hours. The diamond used was natural diamond of a size not exceeding 15 microns at weight percentages not exceeding 2%. This ball milling
20 was conducted dry, i.e. in the absence of a lubricant or solvent. Although this produces an environment that is difficult to control, there is no subsequent need for a powder drying phase. The ball milling of powders in the absence of a lubricant or solvent is known in the field.

25 In the next step, the graded powder is cold pressed to form a green compact that is subsequently sintered in a two stage process. The compact is heated in a reducing atmosphere of hydrogen and at 750 degrees centigrade for 8 hours. It is then cooled, transferred to a vacuum furnace and heated to a temperature of up to 1325 degrees centigrade for 8 hours to form the finished article comprising tungsten
30 carbide cobalt and diamond in a homogenous mixture.

It was found that if the mean diameter of the diamond particles added to the matrix exceeded 20 microns, they acted as a heat sink, absorbing and radiating heat quicker

than the rest of the material. This creates a tendency for the ultra fine tungsten carbide particles in the immediate vicinity of the diamond particles to react with the diamond causing them to dissolve and re-crystallise as much larger particles. For example, fine sub-micron grains of tungsten carbide could re-crystallise as much
5 larger particles up to sizes of 6-8 microns. The re-crystallisation of the fine tungsten carbide particles as larger particles has the consequence of forming localised, segregated pools of surplus cobalt. This effect is thought to be thermochemical in nature and results in a reduction of the compact wear resistant characteristics because a cobalt pool in the tungsten carbide matrix acts as a weak
10 point, reducing the hardness and loosening tungsten carbide particles in the matrix. However, when the diamond particles are of a mean size lower than 15 microns, the re-crystallisation of tungsten carbide particles and so the formation of cobalt pools, with its consequential effects, have been found to be absent.

15 Confirmation of the above analysis can be confirmed by determining the density of the resulting product. As diamond has a much higher density than graphite, a substantially lower density would be the expected result if graphite pools are present, i.e. if the expected back reaction, explained in more detail above, had occurred. A measurement of the density of the article also indicates whether any
20 gas pockets in the green powder compact have been removed as the presence of these would reduce the density of the final product.

The results in table 1 show a comparison of the density of two samples, one having no diamond added and the other having 1% diamond. As can be seen, the
25 determined density as a result of these tests remains very close to the theoretical maximum density which is calculated by proportional summation of the known absolute material density values of the constituents of the product, thereby demonstrating that the formation of graphite does not occur. In Table 1, the percentage value of ρ_{ACH}/ρ_{TH} is shown, where ρ_{ACH} is the achieved product density,
30 and ρ_{TH} is the theoretical maximum product density. All of the values are very close to 100%, indicating a successful compacting and sintering process. It is only because diamond has a lower material density than tungsten carbide, that the sample

containing diamond has a slightly lower density value than that which contains 0% diamond.

It can also be seen from Table 1 that the hardness value achieved with the diamond
5 doped material of the invention is significantly greater than that of the known tungsten carbide compound without any added diamond.

Diamond Added	Resulting Product Density (ρ_{ACH})	% ρ_{ACH}/ρ_{TH}	Hardness of Product
0%	14.51 g/cm ³	99.97	1540-1600 HV
1%	13.61 g/cm ³	96.69	1770 HV

Table 1: Product material values

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A drill bit, having an insert manufactured in accordance with the invention and brazed into a milled pocket in the tip, was tested against two known standard tungsten carbide drill bits for wear resistance and performance. Two types of tests were performed; the first involved repeated drilling of 1 inch holes in a masonry
15 block using a cordless hand-drill, starting with a fully charged battery, until the battery went flat; the second involved repeated drilling of 1 inch holes in masonry blocks using a 240 volt mains-powered hand-drill, until the tip of the drill was worn out or chipped. The respective results of these tests are shown in Tables 2 and 3. Both show that the diamond-doped drill bit of the invention far out-performs the
20 drill bit of the same WC/Co proportional mixture without diamond added, and also that of the drill bit with a higher WC:Co proportion (94:6), which industry standard knowledge would assume would fair better than a 90:10 mix compound drill.

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Drill Bit	Start Diameter/mm	End Diameter/mm	No. Holes Drilled
0% diamond WC:Co = 94:6	6.70	6.67	41
1% diamond WC:Co = 90:10	6.32	6.30	69

Table 2: Cordless drill test results

The results in table 2 illustrate that the drill bit of the invention is by far more efficient than a standard drill bit that did not have a diamond-doped tungsten carbide insert, as it was able to bore considerably more holes with the given amount of energy (a fully charged battery).

Drill Bit Tested	Start Diameter/mm	End Diameter/mm	No. Holes Drilled
0% diamond WC:Co = 90:10	6.84	6.80	30
0% diamond WC:Co = 94:6	6.64	6.64	16
1% diamond WC:Co = 90:10	6.10	6.08	74

Table 3: Mains-powered drill test results

Table 3 clearly shows that the wear resistance of the material of the invention is significantly greater than that of WC/Co without diamond doping, as the drill bits of known material wore down or chipped long before the drill bit having a cutting insert in accordance with the present invention.

It will be appreciated from the foregoing that the present invention provides an improved composite article for use in the manufacture of cutting inserts that has wear resistance intermediate that of standard tungsten carbide cutting inserts and considerably more expensive PCD cutting inserts.

Many modifications and variations of the invention falling within the terms of the following claims will be apparent to those skilled in the art and the foregoing description should be regarded as a description of the preferred embodiments only.

Claims

1. A cemented carbide composite article formed from particles of tungsten carbide and particles of diamond dispersed in a matrix of cobalt, wherein the percentage weight of diamond particles in the article does not exceed 2%.
2. A composite article according to claim 1, wherein the particles of diamond each have a diameter less than 15 microns.
3. A composite article according to claim 2, wherein the particles of diamond each have a diameter between 2 and 10 microns.
4. A composite article according to claim 2 or 3, wherein the particles are substantially spherical.
5. A composite article according to any preceding claim, having a hardness of between 1600 and 1800HV.
6. A composite article according to any of claims 1 to 4, wherein the proportion of tungsten carbide (WC) to Cobalt (Co) is 9:1.
7. A composite article according to claim 6, having a hardness of approximately 1770HV.
8. A composite article according to any preceding claim, wherein the diamond particles are synthetic industrial diamond powder.
9. A composite article according to any preceding claim, wherein the diamond particles are uniformly dispersed throughout the article.
10. A cutting insert for a cutting tool incorporating a composite article according to any preceding claim.

11. A method of manufacturing a composite article comprising the steps of adding diamond particles to a blend of tungsten carbide and cobalt grains at a percentage weight of diamond not exceeding 2% and pressing and sintering the
5 resulting powder to form the compact.
12. A method according to claim 11, wherein the sintering step comprises the steps of:
- a) heating the resulting compact in a reducing atmosphere;
 - 10 b) cooling the compact and,
 - c) subsequently heating the compact in a vacuum furnace.
13. A method according to claim 11 or 12, including the step of simultaneously
15 precipitating cobalt and tungsten carbide alloyed together to form a pre-mixed and pre-alloyed blend of tungsten carbide and cobalt grains.
14. A method according to any of claims 11 to 13, wherein the blend of WC and Co is ball milled with the diamond particles prior to sintering.
- 20 15. A method according to claim 13, whereby the ball milling step is carried out for 72 hours.
16. A method according to claim 12, wherein step (a) includes the step of
25 heating the article to 750° C in a reducing Hydrogen (H₂) atmosphere.
17. A method according to claim 16, wherein the composite article is heated for up to 12 hours.
- 30 18. A method according to claim 12, wherein step (c) involves heating the article in a vacuum furnace to 1375 degrees centigrade.
19. A method according to claim 18, wherein the article is heated up to 16 hours.

20. A method according to any of claims 11 to 19, wherein the method steps are carried out at atmospheric pressure.
- 5 21. A composite article substantially as hereinbefore described.
22. A method of manufacturing a composite article substantially as hereinbefore described.
- 10 23. A cutting insert substantially as hereinbefore described.

Amendments to the claims have been filed as follows

1. A method of manufacturing a composite article comprising the steps of adding diamond particles to a blend of tungsten carbide and cobalt grains at a percentage weight of diamond not exceeding 2% and pressing and sintering the resulting powder to form the compact, wherein said steps are carried out at atmospheric pressure.
2. A method according to claim 1, wherein the sintering step comprises the step of heating the resulting compact in a reducing atmosphere.
3. A method according to claim 2, wherein the sintering step further comprises the steps of:
 - a) cooling the compact and,
 - b) subsequently heating the compact in a vacuum furnace.
4. A method according to any preceding claim, including the step of simultaneously precipitating cobalt and tungsten carbide alloyed together to form a pre-mixed and pre-alloyed blend of tungsten carbide and cobalt grains.
5. A method according to any preceding claim, wherein the blend of WC and Co is ball milled with the diamond particles prior to sintering.
6. A method according to claim 5, whereby the ball milling step is carried out for 72 hours.
7. A method according to claim 2, wherein the step of heating the compact in a reducing atmosphere comprises heating the article to 750° C in a reducing Hydrogen (H₂) atmosphere.
8. A method according to claim 7, wherein the composite article is heated for up to 12 hours.

9. A method according to claim 3, wherein step (b) involves heating the article in a vacuum furnace to 1375 degrees centigrade.
- 5 10. A method according to claim 9, wherein the article is heated up to 16 hours.
11. A cemented carbide composite article manufactured in accordance with the method of any of claims 1 to 10.
- 10 12. A composite article according to claim 11, wherein the particles of diamond each have a diameter less than 15 microns.
13. A composite article according to claim 12, wherein the particles of diamond each have a diameter between 2 and 10 microns.
- 15 14. A composite article according to any of claims 11 to 13, wherein the particles are substantially spherical.
15. A composite article according to any of claims 11 to 14, having a hardness of
20 between 1600 and 1800HV.
16. A composite article according to any of claims 11 to 15, wherein the proportion of tungsten carbide (WC) to Cobalt (Co) is 9:1.
- 25 17. A composite article according to claim 16, having a hardness of approximately 1770HV.
18. A composite article according to any of claims 11 to 17, wherein the diamond particles are synthetic industrial diamond powder.
- 30 19. A composite article according to any of claims 11 to 18, wherein the diamond particles are uniformly dispersed throughout the article.

20. A cutting insert for a cutting tool incorporating a composite article according to any of claims 11 to 19, manufactured in accordance with any of the method steps of claims 1 to 10.
- 5 21. A composite article substantially as hereinbefore described.
22. A method of manufacturing a composite article substantially as hereinbefore described.
- 10 23. A cutting insert substantially as hereinbefore described.



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Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.T): -

Int Cl (Ed.7): C22C

Other: Online: PAJ, WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X	GB 2123439 A (INSTITUT) - page 4 lines 15-17.	1,11 at least
X	GB 705844 (SANVIKENS) - page 1 lines 56-64.	1,11 at least
X	JP 080109431 A (READ) - WPI Abstract Accession No. 96-264004/31 and the PAJ abstract.	1,11 at least
X	JP 070157837 A (HITACHI) - WPI Abstract Accession No. 95-252577/33 and the PAJ abstract.	1,11 at least
X	US 5128080 (JUREWICZ) - the whole specification, especially column 3 lines 13-14, 17 & 29-31.	1 at least
X	US 4525178 (HALL) - the whole specification, especially column 9 lines 27-30.	1,11 at least

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.